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SIMULATION OF HD REACTIVITY
I. COMPETITION RATES OF OXIDATION OF HD WITH SIMULANTS

Yu-Chu Yang, Ph.D.

PHYSICAL PROTECTION DIRECTORATE

Linda L. Szafraniec
William T. Beaudry

RESEARCH DIRECTORATE

Franklin A. Davis, Ph.D.

DREXEL UNIVERSITY
Philadelphia, PA 19104

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Yang, Yu-Chu, Ph.D.; Szafraniec, Linda L.; and Beaudry, William T. (CRDEC); and Davis, Franklin A., Ph.D. (Drexel University)

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13. ABSTRACT (Maximum 200 words)

The competition rates of oxidation of 14 sulfide simulants relative to HD were determined quantitatively in $CDCl_3$ to 20 °C. N-Sulfonyloxaziridine, which selectively oxidized sulfides to the corresponding sulfoxides in less than 2 min, was used as the standard oxidant. The competition rates increased with the nucleophilicity of the sulfur atom. The nucleophilicity of the bivalent sulfur, in turn, was controlled by the electronic effect of the substituent groups in the molecule. Most sulfides examined were more nucleophilic than HD, consisting of two strongly electron-withdrawing 2-chloroethyl groups. The hydrolysis rate of the sulfides determined previously followed the same trend, because the rate-determining step was neighboring sulfur-assisted formation of an ethylenesulfonium ion, the stability of which also depends on the same electronic effect of the substituent group. Futhermore, the competition rates were useful in predicting the rate of production of dimeric sulfonium salts from the hydrolysis of 2-chloroethyl sulfides.

14. SUBJECT TERMS

Competition rate	Oxidation	HD
Sulfides	Hydrolysis rate	Sulfoxides
N-Sulfonyloxaziridine	2-Chloroethyl sulfides	

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PREFACE

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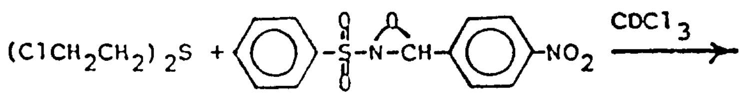
I. COMPETITION RATES OF OXIDATION OF HD WITH SIMULANTS

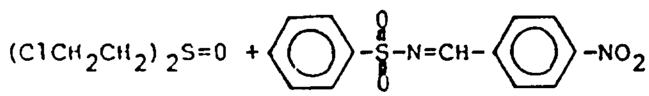
1. INTRODUCTION

The fast, selective oxidation of sulfides by N-sulfonyloxaziridines (OXA), shown in compound I or in equation 1, to sulfoxides in organic solvents has been reported by Davis and co-workers in a series of publications.[1,2] It is proposed that nucleophilic attack by sulfur on the oxygen, which is in a strained, three-membered ring structure, is the oxidation mechanism.[3] The oxidation agent is reduced by the sulfide to an imine (IV or IMN) shown in equation 1. In this study, the oxidation of HD (II) by OXA to HD sulfoxide (III) was investigated at 20 °C in $CDCl_3$ and compared with the oxidation of 14 sulfide simulants. Proton and ^{13}C nuclear magnetic resonance (NMR) spectroscopy were used to measure the reaction rates and to identify the products. Additional product identification was accomplished by gas chromatography/mass spectrometry (GS/MS).

As expected, the oxidation rates of HD and the sulfide simulants by OXA at 20 °C were too fast to be accurately measured. Consequently, the competition rate of oxidation between HD and each of the sulfide simulants was determined from the ratio of the oxidation products. These rates are useful for predicting the oxidation potential of HD from simulant data for other oxidation reactions with the same mechanism.



II I (OXA)

 (1)

III IV (IMN)

2. EXPERIMENTAL PROCEDURES

2.1 Materials.

The HD was a Chemical Agent Standard Analytical Reference Material (CASARM) sample. The sulfide simulants were distilled products from Fairfield Chemical Company (Blythewood, NC) and Aldrich Chemical Company (Milwaukee, WI). The $CDCl_3$ was obtained from MSD Isotopes, Merck, (St. Louis, MO). Professor F. A. Davis, Drexel University (Philadelphia, PA), supplied OXA. All of the above compounds were >95% pure by ^1H and/or ^{13}C NMR and were used as received.

2.2 NMR Measurement of Competition Rate.

Equal molar amounts (0.1 M) of HD and the sulfide simulant were dissolved in $CDCl_3$ in an NMR tube. A ^1H NMR spectrum of the mixture was obtained using 1 pulse and a 90° flip angle with a Varian XL-200 Fourier Transform Nuclear Magnetic Resonance (FTNMR). The ratio, S, of the integrated area of the simulant to the HD (ca. 1.00 ± 3%), was obtained. An equimolar amount of OXA (0.1 M) was subsequently added to the same mixture. The NMR tube was shaken to mix the reactants, allowing the reaction to occur. A ^1H NMR spectrum of the final reaction mixture was obtained in the manner described above.

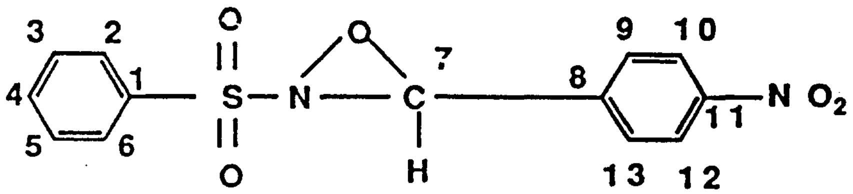
The spectrum was analyzed for the amounts of each reactant remaining and each sulfoxide produced. The ratio of the sulfoxide products, Q, divided by S is calculated as the competition rate, r, of the simulant to HD. In cases where the simulant reacted an order of magnitude faster than HD, the simulant consumed almost all of the OXA to produce the sulfoxide. Therefore, the competition rate of the simulant relative to another sulfide of an intermediate reactivity (usually $CH_3SCH_2CH_2Cl$) was determined instead. This competition rate was then converted to that relative to HD based on the competition rate of $CH_3SCH_2CH_2Cl$ to HD. Various combinations of the two sulfide reactants were tested to ensure that consistent results were obtained and that the calculated r values remained the same. The maximum error in the integrated ^1H areas and in the accuracy of the competition rates reported in Tables 2 and 3 was 5%.

3. RESULTS AND DISCUSSION

3.1 Oxidation of HD by OXA.

To a solution of 5.3×10^{-2} M HD in $CDCl_3$, an excess amount of OXA was added so that the molar ratio of OXA to HD was 1.9:1.0. At 2 min after mixing, all of the HD was converted to one product, HD sulfoxide (III) as detected by ^{13}C NMR ($OSCH_2$, 55.1 ppm and CH_2Cl, 36.7 ppm). A second sample containing about 0.2 M HD and 0.1 M OXA was prepared. Immediate ^{13}C NMR analysis of the sample showed that 45% of the initial HD reacted to produce HD sulfoxide exclusively. All of the OXA was reduced to an imine. Therefore, the stoichiometry of HD oxidation by OXA shown in equation 1 was determined. The oxidation rate of HD was as fast as that reported for most sulfides at ambient temperatures.[1] Although IMN was the only product from OXA, subsequent hydrolysis of IMN to an aldehyde and a sulfonamide was detected after about 2 hr because of a trace amount of water present in the solvent. The ^{13}C NMR shift assignments of OXA, IMN, and the hydrolysis products of IMN in $CDCl_3$ are presented in Table 1. Note the distinctly different ^{13}C NMR shifts of the carbon atoms (C_7) in OXA (74.6 ppm $\overset{O}{HC-N}$) and in IMN (167.9 ppm HC=N). The ^1H NMR shifts of the protons adjacent to the two carbons were also very different: 5.60 ppm in OXA and 9.15 ppm in IMN.

Table 1. Tentative ^{13}C NMR Assignments of OXA and its Reaction Products in $CDCl_3$ (in ppm)



	OXA	IMN	p-Nitrobenz-aldehyde	Benzene Sulfonamide
C_1	137.2*	137.2*		140.0*
C_2	129.4	128.3		126.3
C_3	129.4	129.4		129.0
C_4	135.4	134.2		132.6
C_5	129.4	129.4		129.0
C_6	129.4	128.3		126.3
C_7	74.6	167.9	190.3	
C_8	134.2*	137.3*	142.2*	
C_9	129.6	132.0	130.4	
C_{10}	123.9	124.2	124.3	
C_{11}	149.8	151.2	151.2	
C_{12}	123.9	124.2	130.4	
C_{13}	129.6	132.0	124.3	

*May be reversed

3.2 Competition Rates of Oxidation.

Because the oxidation mechanism is nucleophilic attack by the sulfur on the oxygen in OXA, the oxidation rate should increase with the nucleophilicity of the sulfur atom of the sulfide. This was demonstrated by the competition rates for a series of sulfides shown in Table 2. Each electron withdrawing 2-chloroethyl group reduces the oxidation rate of the sulfide about five fold when HD, 2-chloroethyl ethyl sulfide (CEES), and ethyl sulfide are compared. Alkyl sulfides oxidize faster than aryl sulfides. However, the steric butyl groups in butyl sulfide have offset their electron-donating power and reduced the reactivity of sulfur relative to that of ethyl sulfide.

In Table 3, the effect of substituent groups on sulfur nucleophilicity in the $RSCH_2CH_2X$ derivatives is illustrated. The competition rates remained almost the same even though the alky group (R) in $RSCH_2CH_2Cl$ increased from C_1 to C_5. Perhaps the increase in electron-donating power from an additional $-CH_2$ group was offset by an increase in the steric hindrance. However, as R became more electron withdrawing, as in HD and the phenyl derivative, the

oxidation rate was significantly reduced. Similarly, as the X substituent changed from Cl to Br to OH, the electron-withdrawing power of X decreased, and the nucleophilicity (reactivity) of the sulfur increased.

As shown in both Tables 2 and 3, the hydrolysis rate of $RSCH_2CH_2X$ (X = Cl or Br) also increased with increasing sulfur nucleophilicity. However, a greater effect on the hydrolysis rate relative to oxidation is observed. This greater effect on the hydrolysis rate is expected because it is determined by an intramolecular nucleophilic attack by the sulfur atom on the carbon atom adjacent to X. Similarly, the yield of the dimer product, resulting from nucleophilic attack by the sulfur on another $RSCH_2CH_2X$ molecule also increased with sulfur nucleophilicity.[4] More than 80% dimer was measured as the final hydrolysis product of $CH_3SCH_2CH_2Cl$ (r of $CH_3SCH_2CH_2OH$ is 2.43); whereas, no dimer was produced from the hydrolysis of $PhSCH_2CH_2Cl$ under the same conditions, indicating that the hydrolysis product, $PhSCH_2CH_2OH$ (r = 0.95), is not a competitive nucleophile relative to water in an excess amount. Futhermore, dimerization with $RSCH_2CH_2Cl$ should be slower than with $RSCH_2CH_2OH$, because the latter is a stronger nucleophile. The decrease in sulfur nucleophilicity with the electron withdrawing power of the R group in $RSCH_2CH_2X$ also suggests that in displacement reactions, an external nucleophile may be more competitive with the sulfur atom in HD than in CEES.[5]

Table 2. Relative Oxidation Reactivities of Sulfides to HD by OXA at 20 °C*

Sulfides	Relative Reactivities	
$(ClCH_2CH_2)_2S$	1.0	(1)
$CH_3CH_2SCH_2CH_2Cl$	4.8	(5.9)
$(CH_3CH_2)_2S$	23.0	(-)
$(nBu)_2S$	9.6	(-)
$(Ph)_2S$	0.96	(-)
$PhSCH_2CH_2Cl$	0.92	(0.095)

*Numbers in parentheses are relative ratios of the measured first-order hydrolysis rates of the $RSCH_2CH_2X$ derivatives.

Table 3. Competitive Rate (r) of $RSCH_2CH_2X$ for OXA in $CDCl_3$ at 20 °C*

$RSCH_2CH_2Cl$		$CH_3SCH_2CH_2X$		$PhSCH_2CH_2X$	
R	r	X	r	X	r
methyl	1.0 (1.0)	Cl	1.0	Cl	0.22 (0.021)
ethyl	1.2 (1.3)	--	--	Br	0.44 (0.16)
iso-propyl	1.2 (1.6)	OH	2.4	OH	0.95 (-)
n-butyl	1.2 (1.9)				
iso-butyl	1.2 (1.2)				
iso-amyl	1.3 (-)				
phenyl	0.22 (0.021)				
2-chloroethyl (HD)	0.24 (0.21)				

*Numbers in parentheses are relative ratios of the measured first-order hydrolysis rates of the $RSCH_2CH_2X$ derivatives.

3.3 Dependence of r on OXA Concentration.

In determining the competition rate, the initial concentration of the common reactant (OXA or C in equations 2 and 3) is usually much smaller than the two competing sulfides [reactants A and B where $(A)_0 = (B)_0$]. If $(C)_0$ is much smaller than $(A)_0$ and $(B)_0$, the concentrations of P_A and P_B are small, then (A) is expected to be close to (B) at all times, because only very small amounts of A and B were reacted to produce P_A and P_B. The calculated r should reflect the ratio of the rate constants only, as shown in equations 2-5:

$$A + C \xrightarrow{k_A} P_A \tag{2}$$

$$B + C \xrightarrow{kB} P_B \tag{3}$$

$$r = \frac{r_A}{r_B} = \frac{k_A\,(A)\,(C)}{k_B\,(B)\,(C)} = \frac{k_A\,(A)}{k_B\,(B)} = \frac{k_A\,[(A)_0-(P_A)]}{k_B\,[(B)_0-(P_B)]} = \frac{(P_A)}{(P_B)} \quad (4)$$

$$r = \frac{k_A\,(A)}{k_B\,(B)} = \frac{k_A(A)_0}{k_B(B)_0} = \frac{k_A}{k_B} \quad \text{for } P_A,\ P_B \ll (A)_0 \text{ and } (B)_0 \quad (5)$$

To test if the r values reported in Tables 2 and 3 were true ratios of the rate constants, the competition rates of $CH_3CH_2SCH_2CH_2Cl$ (CEES) with $CH_3SCH_2CH_2Cl$ (CEMS) over OXA concentrations from 0.02 to 0.1 M were determined. In this case, the two sulfide reactants (A and B) happened to be close in their reactivities towards OXA. The result is shown in Table 4. The result clearly shows that within experimental error, the competition rate of CEMS to CEES is constant. In the second case, two sulfides of significantly different oxidation reactivities were also examined against a larger range of OXA concentrations. The two sulfides were CEMS and $PhSCH_2CH_2Cl$ (CEPS), which oxidize at about the same rate as HD (Table 2). In the experiments where the amount of sulfoxide produced from the CEPS was very small because of a small OXA concentration, long hours of FTNMR accumulation (overnight or over a weekend) were necessary to improve the signal-to-noise ratio and the accuracy of the integraded area of sulfoxide. Furthermore, ^{13}C NMR had to be used to detect and measure the sulfoxide product from the CEPS, because the ^{1}H NMR spectra of the reaction mixture were too overlapped for accurate quantitation of the trace amount of sulfoxide product. Again, the competition rates shown in Table 5 are reproducible within the errors of the experimental method. In summary, the competition rates presented in Tables 2 and 3 are independent of the initial concentration of OXA and represent the ratio of the two second order rate constants k_B/k_A.

Table 4. Competition Oxidation Rate vs. Initial OXA Concentration at 20 °C in $CDCl_3$

A $(CEMS)_0$,M	B $(CEES)_0$,M	C $(OXA)_0$,M	x_A[a]	x_B[a]	r[b]
0.11	0.10	0.11	0.47	0.53	1.1
0.10	0.10	0.085	0.46	0.54	1.2
0.10	0.10	0.055	0.46	0.54	1.2
0.10	0.10	0.017	0.46	0.54	1.2

[a] x_A is measured conversion of CEMS to sulfoxide, x_A = (sulfoxide)/$(CEMS)_0$
x_B is measured conversion of CEES to sulfoxide, x_B = (sulfoxide)/$(CEES)_0$

[b] $r = x_B/x_A$

Table 5. Competition Oxidation Rate vs. Initial OXA Concentration at 20 °C in $CDCl_3$

A $(CEMS)_0$	B $(CEPS)_0$	C $(OXA)_0$	x_A[a]	x_B[a]	r[b]
0.10	0.10	0.097	0.86	0.14	0.16
0.10	0.10	0.054	0.82	0.18	0.22
0.10	0.093	0.026	0.82	0.18	0.22
0.10	0.10	0.004	0.78	0.22	0.28
0.10	0.10	0.002	0.83	0.17	0.21

[a] x_A is measured conversion of CEMS to sulfoxide, $x_A = (\text{sulfoxide})/(\text{CEMS})_0$
x_B is measured conversion of CEPS to sulfoxide, $x_B = (\text{sulfoxide})/(\text{CEES})_0$

[b] $r = x_B/x_A$

Previously, Davis et al[6] reported r by measuring the isolated yields of the two sulfoxide products from the reaction mixture. We believe greater errors can result from this measurement because some of the sulfoxide products might not be recovered completely. Particularly, the authors reported that CEPS had about the same reactivity as CEES and CEMS. NMR appears to be a better method because all of the products can be observed and measured directly in the solvent.

3.4 Comparison of OXA with Sodium Hypochlorite.

Because HD is oxidatively degraded by decontaminants containing hypochlorite (^-OCl), it is important to compare the reaction mechanism of OXA with that of ^-OCl before recommending OXA as a substitute for ^-OCl in the decontamination of HD. The reaction of hypochlorite with HD and CEES was examined using ^{13}C NMR. As shown in Table 6, in addition to the expected oxidation products (sulfoxide and sulfone), an elimination reaction also occurred by reaction of the HD with NaOH to produce the vinyl sulfide. In an initially two-phase mixture of HD and 5% NaOCl solution, vinyl sulfoxide, ether/alcohol, and carbonyl groups were also identified in the final one-phase solution after 18 hr. This indicates that the reaction rate and mechanism are very complicated.[7] Furthermore, more than 1 mol of the ^-OCl was consumed for each mole of HD that reacted. Therefore, hypochlorite is not a stoichiometrically efficient oxidant for HD. The complicated kinetics and mechanism make it impossible to determine a competition rate for the hypochlorite ion.

Table 6. Oxidation of $RSCH_2CH_2Cl$ by Excess NaOCl at 20-25 °C

R	Reaction Condition and Time	NMR	Identification of Products
CH_3*	PEG-one phase t=0	^1H NMR:	complex products, sulfoxide + sulfone + vinyl sulfide + other unidentified products
C_2H_5	two phases t=18 hr	^{13}C NMR:	4-6 products, sulfoxide + sulfone + vinyl sulfide + vinyl sulfoxide
ClC_2H_4	two phases t=18 hr	^{13}C NMR:	5-10 products, sulfoxide + sulfone + vinyl sulfide + vinyl sulfoxide + ether/alcohol + carbonyl groups

*Reference 7, PEG is polyethylene glycol, a phase-transfer agent.

4. CONCLUSION

In a neutral organic medium ($CDCl_3$), the reactivity of a sulfide molecule towards a non-nucleophilic oxidant such as OXA increased with the nucleophilicity of the sulfur atom. The sulfur atom in HD was a weaker nucleophile than the sulfur in most simulants; consequently, HD was oxidized at a slower rate than most of the simulants. An excellent oxidant in converting HD selectively to HD sulfoxide is OXA, because the reaction is a simple bimolecular mechanism; the reaction rate is instantaneous; only 1 mol of OXA is consumed per mole of HD reacted; and the sulfoxide product has been considered a nontoxic material.

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